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CHEMISTRY OF ORGANOSILICON COMPOUNDS

CXC *. AN ESR STUDY OF CONFORMATIONAL TRANSMISSION IN BIS(TRIMETHYLSILYLMETHYL)METHYL AND RELATED RADICALS **

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Summary

Static conformations and the dynamic behavior of the radicals $(MCH_2)_2\dot{C}X$ (where $M = SiR_3$, GeR_3, or SnR_3; $X = H$, CH_3, or $OSiMe_3$) have been investigated by ESR. At the preferred conformation, the two metal groups almost eclipse the singly-occupied carbon *p*-orbital and are located on the opposite sides of the CH_2CXCH_2 plane. The barriers for the flip-flop motion, evaluated by the line-shape analysis of the temperature-dependent ESR spectra, are closely related to those for the metal-group rotation about the $C(\alpha)$–$C(\beta)$ bond.

Introduction

ESR studies of $R_3XCH_2\dot{C}H_2$ type radicals (where X = Si, Ge, or Sn) [1,2] have revealed that these radicals exist in a preferred conformation in which the metal substituent occupies an eclipsed position relative to the singly-occupied carbon *p*-orbital and optimally located to interact with it; the odd electron delocalizes onto the carbon–metal bond by hyperconjugation. Rotational barriers of the related radicals $CH_2{=}CH{-}\dot{C}H{-}CH_2XR_3$, have been determined by analysis of the temperature-dependent ESR spectra [3].

Current interests in a conformational transmission process [4] involving a gear system have prompted us to investigate the conformational effects induced by two

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β-metal-substituents on the carbon-centered radicals $(MCH_2)_2\dot{C}X$ (where M = SiR_3, GeR_3, or SnR_3; X = H or CH_3) by ESR spectroscopy. Since the suitable dispositions of the two metal substituents may be determined primarily by hyperconjugation rather than steric factors, these systems can be a model for a unique conformational transmission process. In an earlier study [5] the related radical, tris(trimethylsilylmethyl)amine radical cation, showed selective ESR line-broadening due to the interconversion between conformations. The dynamic ESR technique was found to be useful to elucidate an intramolecular interconversion by such a gear system with a relatively small barrier.

After completion of the present work we have learned of a related report on similar radicals [6], which has stimulated us to publish our results.

Results and discussion

Generation and ESR spectra of radicals

A series of symmetrically 1,3-disubstituted 2-propyl radicals and related radicals (**1a**–**1g**) were generated by photolysis of a mixture of a suitable Group IVB-substituted olefin, the corresponding Group IVB metal hydride (or hexamethyldistannane for **1c**), di-t-butyl peroxide (DTBP), and cyclopropane. At low temperatures the ESR spectra of these radicals showed two sets of triplets due to two sets of two β-methylene protons which split further into a doublet, due to an α-proton in the case of **1a**–**1d**, or a quartet due to three methyl protons in **1e** and **1f**. When the temperature was raised, these ESR spectra showed selective line-broadening and the two sets of triplets coalesced into a quintet due to four equivalent β-protons. The temperature-dependent ESR spectra of **1a** are shown in Fig. 1. The values and assignments of the observed hyperfine splitting constants (hfsc's) of these radicals at the lowest and highest temperatures are listed in Table 1. Details of the ESR analysis are discussed in the following sections.

(1)

(1)

(1a, X = H, M = $SiMe_3$;
1b X = H, M = $GeMe_3$,
1c X = H, M = $SnMe_3$,
1d, X = H, M = Si_2Me_5;
1e, X = CH_3, M = $SiMe_3$;
1f; X = CH_3, M = Si_2Me_5;
1g, X = $OSiMe_3$, M = $SiMe_3$)

ESR parameters and static conformations at low temperatures

Two different methylene proton hfsc's were observed for radicals **1a**–**1f** at the lowest temperatures, as shown in Table 1. These facts indicate that the two C–H bonds of each methylene group of these radicals have a different orientation relative to the singly-occupied molecular orbital (SOMO). The location of the methylene protons relative to the direction of the SOMO can be determined by the following procedure. The dihedral angle, θ, between a β-CH bond and the SOMO can be estimated by eq. 2, which is deduced from the simple $\cos^2\theta$ rule [7] for the β-proton hfsc (eq. 3) combined with the McConnell relationship [8] for the α-proton hfsc (eq. 4), where ρ is the π spin density on the α-carbon, and B and Q are constants. The value of B/Q for the 1,3-disubstituted 2-propyl radicals **1a**–**1d** was taken to be

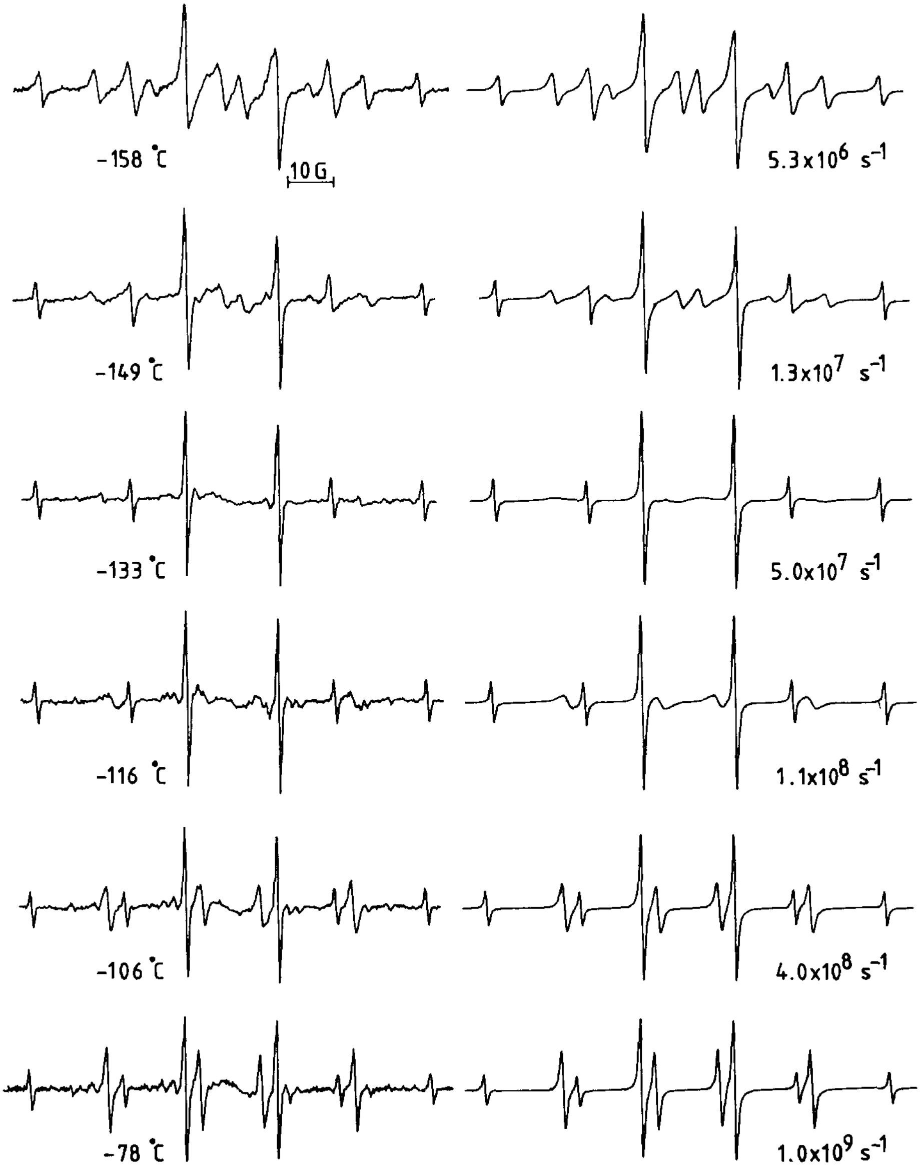


Fig. 1. Experimental ESR spectra of **1a** at various temperatures (left) and the simulated spectra obtained with the designated rate constants (right).

TABLE 1

^{1}H HFSC'S OF 1,3-DISUBSTITUTED 2-PROPYL AND RELATED RADICALS, $(MCH_2)_2\dot{C}X$, AT THE LOWEST AND HIGHEST TEMPERATURES USED

Radical	M	X	Temp (°C)	a(X) (G)	$a(\beta)$ (G)		$\bar{a}(\beta)$ (G)
	H	H [a]	−162	22.15	–		24.74
1a	$SiMe_3$	H [b]	−158	20.15	19.65	12.05	15.85
			−78	20.20	–		16.99
1b	$GeMe_3$	H	−152	19.68	16.42	12.80	14.61
			−86	19.78	–		15.39
1c	$SnMe_3$	H	−131	18.66	14.67	13.05	13.86
			−80	18.55	–		14.10
1d	$SiMe_2SiMe_3$	H	−125	20.11	21.43	10.46	15.95
			−72	19.83	–		16.75
	H	CH_3 [a]	−157	–	–		22.71
1e	$SiMe_3$	CH_3	−126	21.63 [c]	15.83	13.10	14.47
			−81	21.85	–		14.68
1f	$SiMe_2SiMe_3$	CH_3	−132	21.80 [c]	16.15	12.43	14.29
			−68	21.65	–		14.59
1g	$SiMe_3$	$OSiMe_3$	−106	–	–		16.60
			−77	–	–		16.85

[a] P.J. Krusic and J.K. Kochi, J. Am. Chem. Soc., 90 (1968) 7155. [b] $a(^{29}Si) = 36.50$ (2 Si at −152 °C), 34.68 (2 Si at −75 °C) G. [c] Methyl proton hfsc.

2.234, estimated from the proton hfsc of the 2-propyl radicals [9] where the averaged $\cos^2\theta$ for the freely-rotating methyl protons is 1/2.

$$\theta = \cos^{-1}(a(\beta)Q/Ba(\alpha))^{1/2} \tag{2}$$

$$a(\beta) = B\rho\cos^2\theta \tag{3}$$

$$a(\alpha) = Q\rho \tag{4}$$

For the 2-methyl-substituted radicals **1e** and **1f**, eq. 2 can be modified to eq. 5, since the value of $a(\alpha)B/2Q$ can be replaced by the observed methyl proton hfsc (a(Me)).

$$\theta = \cos^{-1}(a(\beta)/2a(\mathrm{Me}))^{1/2} \tag{5}$$

The angles θ and θ' calculated thus for two different methylene protons are shown in Table 2. A residual dihedral angle, ψ, between a carbon–metal bond and the SOMO, is evaluated from the θ and θ' values by assuming that the C(α)–C(β)–M planes bisect the H(β)–C(β)–H′(β) angles, and is also shown in Table 2. The definitions of these angles are illustrated in Fig. 2.

The ψ-values determined for **1a**–**1c** are very similar to those for $CH_2{=}\dot{C}HCH_2M$ reported by Kawamura et al. [3], where ψ decreases in the order of M = SiR_3, GeR_3, and SnR_3. Although these results support the conclusion that the eclipsed conformation may be preferred due to the effective hyperconjugation by the β-metal substituents in the radicals, it should be noted that ψ is also sensitive to the steric bulk of substituents at C(α); ψ is decreased from 5.1 to 1.9° and from 7.4 to 2.6° by introducing a methyl substituent at C(α) in **1a** and **1d**, respectively. Each M group may thus be taken to incline to the less crowded side near to the X group of **1a**–**1f**, as depicted in Fig. 2.

TABLE 2

DIHEDRAL ANGLES IN THE PREFERRED CONFORMATIONS OF 1,3-DISUBSTITUTED 2-PROPYL AND THE RELATED RADICALS $(MCH_2)_2\dot{C}X$ [a]

Radical	M	X	Temp (°C)	θ' (deg.)	θ (deg.)	ψ (deg.) [b]	Method
1a	$SiMe_3$	H	−158	48.6	58.8	5.1	*c*
1b	$GeMe_3$	H	−152	52.3	57.3	2.5	*c*
1c	$SnMe_3$	H	−131	53.6	56.0	1.2	*c*
1d	Si_2Me_5	H	−125	46.3	61.1	7.4	*c*
1e	$SiMe_3$	CH_3	−126	53.1	56.9	1.9	*d*
1f	Si_2Me_5	CH_3	−132	52.5	57.7	2.6	*d*

[a] The detailed procedure to determine the dihedral angle is described in the text. [b] ψ Is defined as $(\theta - \theta')/2$. [c] $\theta = \cos^{-1}(a(\beta)Q/a(\alpha)B)^{1/2}$, where $B/Q = 2.234$. [d] $\theta = \cos^{-1}(a(\beta)/2a(\text{Me}))^{1/2}$.

Although the ESR parameters alone cannot indicate the relative location of the two M groups about the C(β)–C(α)–C(β)′ plane, the *syn*-conformation of the two groups may be much less favorable than the *anti*-conformation with C_2 local symmetry. The static conformations of **1a**–**1f** are thus concluded to be *A*, as shown in Fig. 2. The satellite spectrum attributed to the splitting by natural silicon-29 in **1a**

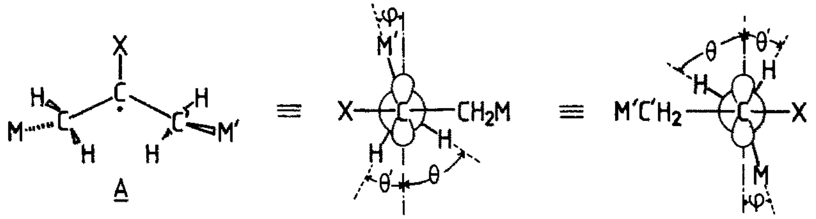


Fig. 2. Definition of the dihedral angles θ, θ′ and ψ, and the preferred rotational conformation of **1**.

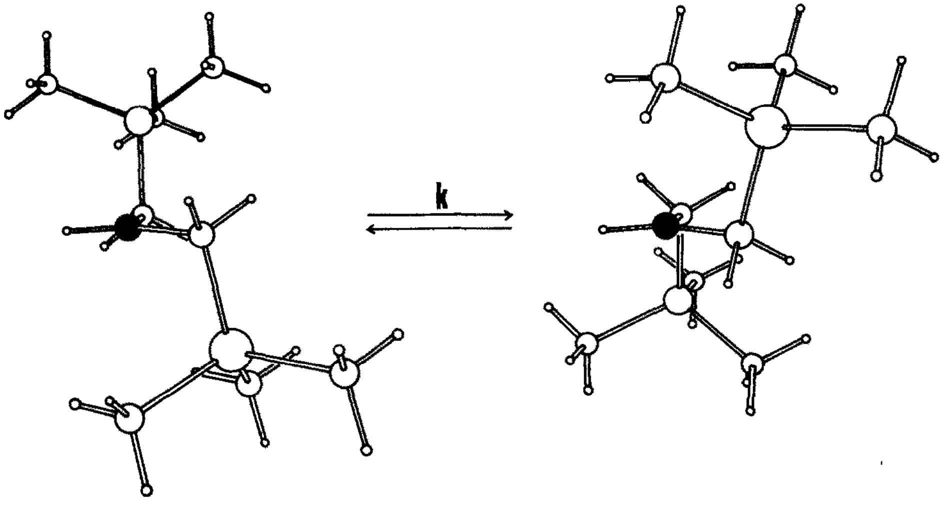


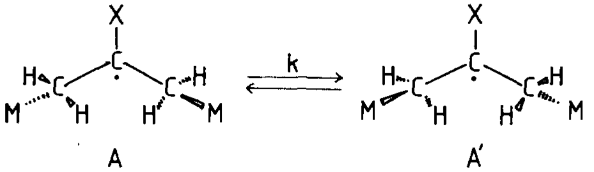
Fig. 3. Perspective view of **1a** at the preferred conformations. The flip-flop motion is represented as the interconversion between the two equivalent conformations.

was observed with a single hfsc of 36.5 G at −152 °C. This relatively large ^{29}Si hfsc, which is comparable to that for $Me_3SiCH_2\dot{C}H_2$ [2], the small negative temperature coefficient ($da(^{29}Si)/dT = -2.36 \times 10^{-2}$ G/K), and the intensity ratio to the main spectra (where the peak-to-peak ratio was 5.6/100), are all compatible with the proposed conformation. A perspective view of **1a** is shown in Fig. 3.

Although **1g** was not observed enough at low temperatures to differentiate the two β-proton hfsc's, the selective line-broadening was appreciable at −106 °C. The averaged β-proton hfsc increased with increasing temperature. These findings are in accord with the equilibrium conformation of **1g** as depicted in Fig. 2.

Dynamic behavior of radicals 1a–1f

The selective line-broadening phenomena of the ESR spectra for **1a**–**1f** are compatible with the idea that the interconversion between the conformation *A* and the equivalent *A′* (eq. 6; see also Fig. 3) occurs with the rates related to the difference in the two β-proton hfsc's. Two different sets of β-protons, (H(1) + H(4) and H(2) + H(3)), should have the same averaged hfsc's by the flip-flop motion between *A* and *A′*. The exchange rates *k* are determined by fitting the experimental spectra to the computer-simulated ones, which are calculated by solving the modified Bloch equations [10]. The ESR spectra of **1a** at various temperatures and the simulated ones are shown in Fig. 1, as a typical example. The Eyring parameters, determined from the plots of $\ln(k/T)$ vs. T^{-1} shown in Fig. 4, are given in Table 3 together with those reported for the related radicals.



(6)

The 1,3-bis(pentamethyldisilanyl)-2-propyl radical **1d** showed a rather unusual temperature dependence. The two-jump model shown in eq. 6 could not be applied to **1d**; the ratio between the first and fourth line was observed to be 1 : 3 at the coalescence point rather than 1 : 4, the disagreement with the expectation from eq. 6. At the lower temperatures, all the lines were broadened. Such behavior is very similar to that of $(MeSCH_2)_2\dot{C}H$, reported by Lunazzi et al. [6]. Although they have discussed the phenomena very extensively by arguing several points, their second explanation, i.e. the freezing of the rotation of M groups around the C(β)–M bonds in $(MCH_2)_2\dot{C}H$, may be more plausible than the others as the origin of the phenomena, since these were observed only when the substituents M had no C_{3v} local symmetry.

Among **1a**–**1c**, the activation enthalpy, as well as the activation free energy of the flip-flop motion, increased with decreasing ψ-values at the static conformation. As suggested from the similar tendency found in substituted butenyl radicals ($CH_2{=}CH\dot{C}HCH_2M$) [3], the barriers of the flip-flop motion should be closely related to those of the M-group rotation in butenyl radicals; the hyperconjugative stabilization at the eclipsed conformation is lost, at least partly, in the transition state of both motions. The flip-flop motion in this system may be regarded as a

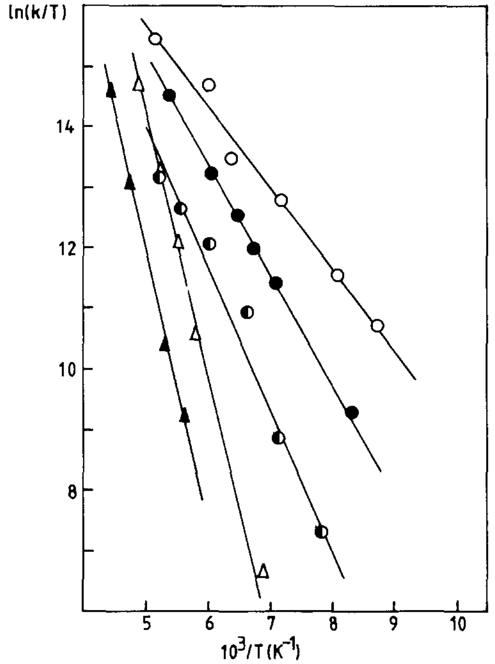


Fig. 4. Plots of ln(k/T) vs. T^{-1} for the flip-flop motion of radicals **1**: (○) **1a**, (●) **1b**, (◐) **1c**, (△) **1e**, and (▲) **1f**.

correlated rotation whose activation energy is controlled by hyperconjugation rather than steric factors. Three possible mechanisms for the motion are shown in Fig. 5; a concerted conrotatory mode (A), a concerted disrotatory mode (B), and a non-concerted correlated mode (C). Modes A and B should be highly unfavorable, since both involve completely synchronous rotation where double hyperconjugation between the two C–M bonds and a p_π SOMO is lost at the same time at the transition states *b* and *c*. Mode C is not synchronous but is still correlated, where one of the two groups rotates from *a* to *d*, then the two groups move concertedly with a conrotatory mode to give *d′*, and then another M group rotates to the final structure *a′*. Mode C is energetically preferred, since the loss of hyperconjugative stabilization at the transition state between *d* and *d′* is only about one half of that in modes A and B.

The substitution of a hydrogen for a methyl at the 2-position of **1a** causes a small increase in the activation free energy ($\Delta G^{\ddagger}$); the difference of $\Delta G^{\ddagger}$ between **1e** and **1a** ($\Delta\Delta G^{\ddagger}$) is ca. 1.3 kcal/mol at −100 °C.

If we estimate the steric repulsion at the transition state from the apparent Van der Waals radii ($r^{\star}$) of H, CH_3, and Me_3Si, which were determined from the study of 2,2′-disubstituted biphenyl systems [11], by using eq. 7 the $\Delta\Delta G^{\ddagger}$ can be estimated as 2.0 kcal/mol at 340 K, which is in good accord with the experimental value.

$$\Delta\Delta G^{\ddagger}_{340\mathrm{K}}(\mathrm{kJ/mol}) = 26\,\Sigma\, r^{\star} + 4.7 \tag{7}$$

Although it is seen that the differences of $\Delta H^{\ddagger}$ as well as $\Delta S^{\ddagger}$ between **1a** and **1e** are very large in contrast to the small $\Delta\Delta G^{\ddagger}$, the unusual effects of the methyl group to the activation parameters are difficult to rationalize; in view of the well-known

TABLE 3

COMPARISON OF THE ACTIVATION PARAMETERS FOR THE FLIP-FLOP MOTION OF RADICALS **1a**–**1f** AND FOR THE HINDERED ROTATION ABOUT THE C(α)–C(β) BOND OF THE SUBSTITUTED BUTENYL RADICALS

Radical	Ea[a]	log A	$\Delta H^{\ddagger}$[a]	$\Delta S^{\ddagger}$[b]	$\Delta G^{\ddagger}_{173K}$[a]
1a	3.0	12.3	2.7	−2.7	3.2
1b	3.9	13.1	3.6	0.54	3.5
1c	4.9	13.8	4.6	3.7	4.0
1e	8.8	18.1	8.5	23.2	4.5
1f	9.4	17.8	9.1	21.6	5.3
$CH_2{=}CH{-}\dot{C}H{-}CH_2SiMe_3$[c]	3.1	12.6			
$CH_2{=}CH{-}\dot{C}H{-}CH_2GeMe_3$[c]	4.0	13.4			
$CH_2{=}CH{-}\dot{C}H{-}CH_2SnMe_3$[c]	4 8	13.0			

[a] kcal/mol. [b] cal mol^{-1} K^{-1}. [c] Ref. 3.

inaccuracies in separating $\Delta G^{\ddagger}$ into $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ [12] we did not attempt to analyze this point further. Nontheless, the mechanism of the flip-flop motion of **1d** and **1e** may be essentially similar to that of **1a**–**1c** since a good linear correlation is observed between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in **1a**–**1e**.

Experimental

Materials

Allyltrimethylsilane, (2-methallyl)trimethylsilane, 2-methallylpentamethyldisilane, allylpentamethyldisilane, allyltrimethylgermane, allyltrimethylstannane, and (2-trimethylsiloxyallyl)trimethylsilane were prepared by the reaction of the corresponding metal chlorides and allyl Grignard reagents. All the materials used were purified by preparative GLC or fractional distillation before use.

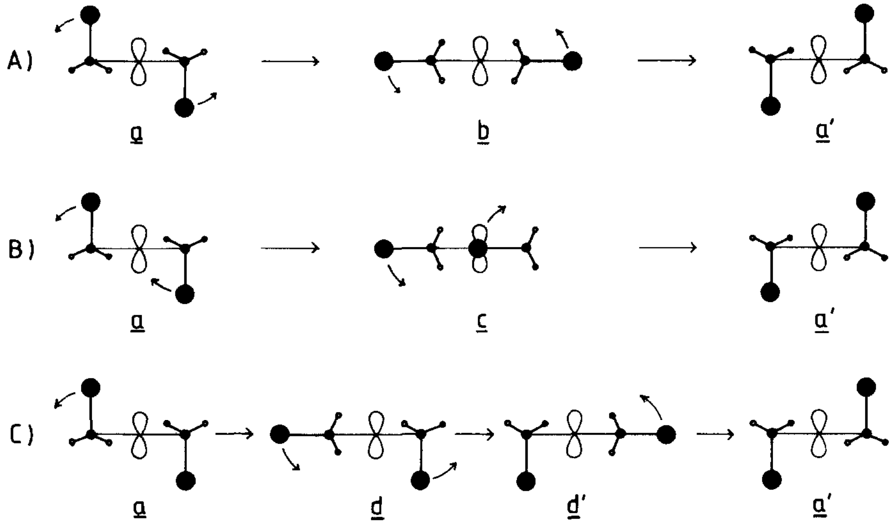
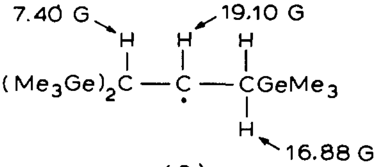


Fig. 5. Possible pathways for the flip-flop motion of radicals **1**: (A) concerted conrotatory mode, (B) concerted disrotatory mode, and (C) non-concerted mode. The circles ⬤, ●, and ∘ designate the M, C, and H atoms, respectively.

ESR Spectroscopy

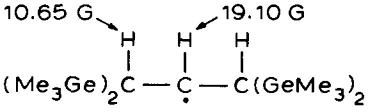
A mixture of the corresponding olefin and metal hydride (or hexamethyldistannane in one case), DTBP, and cyclopropane (v/v 1 : 1 : 0.5 : 0.25) was degassed and irradiated, by a 500 W Ushio super-high pressure mercury lamp, in the cavity of a Varian E-12 ESR spectrometer. Temperatures were controlled by a Varian variable-temperature apparatus, and calibrated by a Cu-constantane thermocouple, to within ±2 °C.

When a mixture of allyltrimethylgermane, DTBP, cyclopropane, and a large excess of trimethylgermane was irradiated, the ESR spectrum of **1b** was contaminated by unexpected signals (assignable to radicals **2** and **3**) under prolonged irradiation. The contamination can be avoided by using a smaller amount of Me_3GeH relative to allyltrimethylgermane. Several experiments to observe the 1,3-bis(trichlorosilyl)-2-propyl radical, using a technique similar to that above, failed. When a 1 : 1 mixture of allyltrimethylstannane and trimethylsilane was under similar conditions, only the 1,3-bis(trimethylstannyl)-2-propyl radical was observed in the temperature range −129 to −77 °C. These observations suggests that abstraction of H and Me_3Sn from the adduct radicals occur rather easily under the conditions [13].



$(Me_3Ge)_2CH-\dot{C}H-CH_2GeMe_3$

(2)



$(Me_3Ge)_2CH-\dot{C}H-CH(GeMe_3)_2$

(3)

Acknowledgments

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